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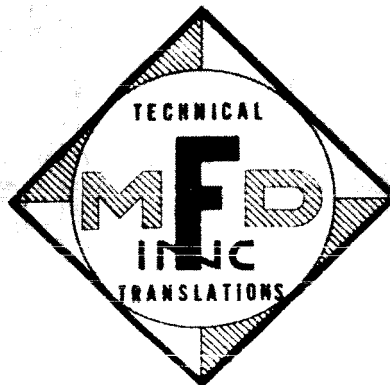
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Use of Molecular Beams for the Radio-Spectroscopic

Study of the Rotational Spectra of Molecules

N. G. BASOV & A. M. PROKHOROV

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Abstract: Methods are developed for using molecular beams to investigate the rotational spectra of molecules. The use of molecular beams permits obtaining narrow spectral lines with a width of ~ 7 kc. and makes possible the study of the rotational spectrum of substances which normally are found in the solid state.

Introduction

The great limitation to the use of the radio-spectroscopic method in the investigation of the rotational spectra of molecules is that only substances in a gasiform state possess rotational spectra. In practice, it is necessary to have vapor pressures, for the substance under investigation, of $\sim 10^{-2}$ mm Hg, since at lower pressures the line intensity decreases. Therefore, in order to investigate the rotational spectra of substances which are solids under normal conditions, it is necessary to heat the absorbing cell of the spectroscopy to that temperature for which the vapor tension of the substance under study would reach $\sim 10^{-2}$ mm Hg. Such a means of investigation leads to a loss in the resolving power of the radio-spectroscopy since the heating of the substance widens the spectral lines because of the Doppler effect and the molecular collisions with the walls of the absorbing cell.

It should be noted that the investigation of solid compounds is of especial interest since sufficiently simple gasiform compounds possessing dipole moments are unknown for many elements. The majority of the solid ionic compounds have large dipole moments, i.e., can be investigated by the radio-spectroscopic method. For example, gasiform compounds are unknown for the rare-earth group of elements which would assist in making possible the determination of the

nuclear moments of these elements.

The width of the spectral lines may be decreased substantially if the microwave absorption is observed not in a gas, as is done in radio-spectroscopy, but in a molecular beam. The line width of a molecular beam, "monochromatic" in terms of velocity, is determined by the time-span of the molecule in the field of microwave radiation. For example, if the length of the flight of the molecule in the field equals 1 cm and the velocity of the molecule is 500 m/sec then the half-width of the line is found to be equal to

$$(1) \quad \Delta\nu = \frac{1}{2\pi\tau} = 8 \text{ kc}$$

where τ is the time of flight of the molecule in the radiation field.

In view of the velocities of the molecules in the beam not being identical, it would appear to be necessary to take the Doppler broadening into account in the beam also. It is possible to get rid of the Doppler line-broadening in a nonmonochromatic-velocity beam of molecules if such waves are excited in the cavity resonator or waveguide for which the phase velocity would be infinite in the direction of beam propagation. This is a result of the frequency displacement, as can be shown, being determined by the ratio of the velocity of the beam molecules to the phase velocity of the waves in the direction of beam propagation.¹

1. Molecular Beam

The number of molecules escaping from a slot source of a molecular beam in one second equals:

$$(2) \quad N = \frac{1}{4} \bar{n} \bar{v} a$$

where $\bar{v} = \sqrt{\frac{8kT}{\pi M}}$ is the average velocity of the beam molecules; \bar{n} is the molecule density within the source of the molecular beam; a is the area of the slot source and M is the molecule mass.

broadening

1. It should be noted that the Doppler broadening of the lines of a gas molecule filling the cavity resonator or waveguide equals the Doppler broadening of the lines of a gas in free space.

The number of beam molecules falling normally on an area S perpendicular to the plane of the slot source equals

$$(3) \quad N_S = \frac{N}{\pi r^2} S$$

where r is the distance between the plane S and the slot source.

The following number of molecules is found from this number of molecules on the rotational level characterized by the quantum number of the rotational momentum J and the vibrational quantum number v :

$$(4) \quad N_{Jv} = N_S \frac{g_J \exp\left(-\frac{E_J}{kT}\right)}{Q_{\text{rot}}} \frac{g_v \exp\left(-\frac{E_v}{kT}\right)}{Q_{\text{vib}}}$$

where E_J is the rotational energy of the molecules; g_J is the statistical weight of the rotational state; Q_{rot} is the rotational statistical sum; E_v is the vibrational energy of the molecules; g_v is the statistical weight of the vibrational state and Q_{vib} is the vibrational statistical sum.

As the beam of molecules passes through a high-frequency field of frequency $\nu = \frac{E_{J+1} - E_J}{h}$, the number of molecules absorbing the energy equals

$$(5) \quad N_{\text{act}} = g_J \left(\frac{N_{Jv}}{g_J} - \frac{N_{J+1v}}{g_{J+1}} \right) \approx N_{Jv} \frac{h}{kT}$$

The last equality holds because $h\nu \ll kT$ for the microwave region.

Therefore, as a consequence of the almost-identical population of the E_J and E_{J+1} rotational levels, only an $\frac{h\nu}{kT}$ part of the molecules out of the total number of the molecules on the E_{Jv} level takes part in the absorption of the microwave energy. We call those molecules which take part in the energy absorption, active molecules.

As a consequence of the molecules in the molecular beam not interacting, a deviation in the molecule equilibrium distribution over the energy levels is not removed.

This yields the possibility of increasing the number of active molecules by separating them according to rotational states. This separation of the molecules according to rotational state can be obtained by passing the molecular beam through an inhomogeneous electric field with field gradient perpendicular to the direction of beam propagation. Because the projection of the effective dipole moment in the direction of the external field depends on the quantum number J and its projection in the external field M_J , the molecules in the various rotational states are deflected differently by the inhomogeneous electric field and, therefore, the molecules in specific rotational states can be separated out. Such a sorting method is used in the resonance method of molecular beams [1]. The use of sorted molecules makes possible increasing the number of active molecules by $\sim \frac{kT}{h\nu}$ times.

The maximum density of the molecules in the beam is determined from the condition that there would not be collisions between the beam molecules during the time the molecules were in the high-frequency radiation field. It can be shown that the mean free path of the molecules in the beam equals approximately the mean free path of molecules in a gas if the density of the gas molecules is equal to the density of the beam molecules.

In using the molecules sorted according to rotational states, the maximum beam density is determined from the condition that there be no collisions between the molecules while in the sorting electric field and in the radiation field.²

2. Sensitivity of the Spectroscope

The spectroscope sensitivity is determined by the noise level of the crystal detector through which the energy absorption of the gas molecules is observed.

2. It should be noted that the gas-kinetic diameter of molecule collisions is less than the microwave diameter of collisions.

Since at low powers, the crystal noise varies slightly with the variation of the power at the crystal, then the sensitivity of the spectroscope increases with the increase of the absolute value of the power absorbed by the molecules. The magnitude of the power absorbed by the molecules is proportional to the power of the high-frequency radiation through which the molecular beam passes if there is no saturation effect.

Let us determine the optimal amount of power of the high-frequency radiation. The probability of a molecule transition from the m state to the n state in the time τ , under the action of radiation, is determined by the formula [2]:

$$(6) \quad W_n^m = 1 - \exp\left(-\frac{\tau}{\gamma}\right)$$

where

$$(7) \quad \frac{1}{\gamma} = \frac{8\pi^2 \rho(\nu) |\mu_n^m|^2}{3h^2(\Delta\nu)}$$

$\rho(\nu)$ is the density of the radiation energy of the high-frequency field; $\Delta\nu$ is the half-width of the spectral lines; μ_n^m is the matrix element of the molecule dipole moment.

The time the molecule remains in the radiation field is determined by the magnitude of τ , the time the beam molecules are in the high-frequency field. The time the molecule remains in a given state is determined by the magnitude of γ which is related to the radiation field density $\rho(\nu)$. If $\gamma < \tau$, then saturation approaches, whereupon the spectral line-width will be determined not by the time τ , but by the life-time of the molecule in the given state, i.e., by γ .

If $\gamma > \tau$, then not all the active molecules take part in the energy absorption during the time they are in the high-frequency field. The optimum value of $\rho(\nu)$ should be chosen so that $\tau \approx \gamma$; hence 43% of the active

Molecules take part in the absorption.³ The maximum possible value of the absorbed energy is obtained when one half the active molecules make a transition from a lower state to a higher.

Thus the optimal density of radiation $\rho_{\text{opt}}(\nu)$ is determined by the equality

$$(8) \quad \gamma = \tau$$

Hence, taking (7) and (1) into account, we obtain

$$(9) \quad \rho_{\text{opt}}(\nu) = \frac{3h^2(\Delta\nu)^2}{4\pi|\mu_n^m|^2}$$

For the $\rho_{\text{opt}}(\nu)$ field density, the beam molecules absorb energy equal to

$$(10) \quad E_{\text{abs}} = 0.43 N_{\text{act}} h\nu$$

It should be noted that $\rho_{\text{opt}}(\nu)$ depends, for transitions between levels with given J , also on M_J , consequently, as $\rho_{\text{opt}}(\nu)$ should be taken some average value of the optimum values for each Zeeman component.

When molecular beams are used the energy density $\rho(\nu)$ which is obtained is considerably less than the energy density in the usual radio spectroscopy, since in the beam case narrower lines are obtained. It is easy to show that for low values of energy flow, use of a superheterodyne receiver gives an undoubted advantage in sensitivity. If the flow of power equals P , then the minimum observable variation in power within the background noise when a superheterodyne receiver is used equals

$$(11) \quad \Delta P = 2 \sqrt{P_n P}$$

where P_n is the noise power.

The magnitude of the noise power for a superheterodyne receiver with the pass band Δf equals

3. It should be kept in mind that at $\tau = \gamma$ the line is broadened by $\Delta\nu' = \Delta\nu\sqrt{2}$.

$$(12) \quad P_n = FkT\Delta f$$

where F is the noise-factor of the receiver.

Let us consider different variations of using molecular beams to study the rotational spectra of molecules.

3. Spectroscope with a waveguide absorbing cell

Let the electromagnetic radiation be propagated along the ox axis in which the ground wave is excited (fig. 1).

According to (9), the optimum power of the energy flow equals

$$(13) \quad P_{opt} = \frac{3h^2 c (\Delta\nu)^2}{4\pi |\mu_n^m|^2} bd$$

where c is the velocity of light.

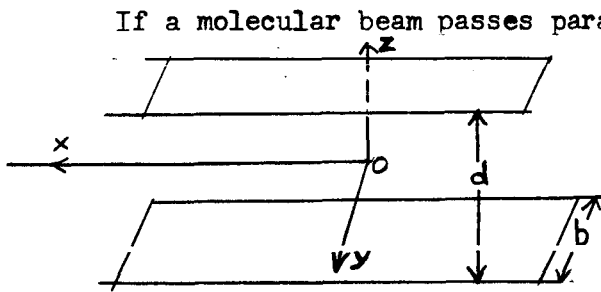


Figure 1

If a molecular beam passes parallel to the oy axis through such a waveguide then the Doppler broadening of the spectral lines will not exist since the phase velocity of propagating the ground wave in this direction is infinite. If a divergent molecular beam is used, then it is necessary that the Doppler broadening

because of the v_x velocity component of the molecule would give a Doppler line width less than the line width related to the time the molecules are in the radiation field, i.e.,

$$(14) \quad v_x < \frac{c}{\pi \gamma \nu_0 \sqrt{2\pi \ln 2}}$$

Therefore, the admissible scattering angle of the beam molecules will be

$$(15) \quad \tan \alpha < \frac{v_x}{v} = \frac{c}{\pi \gamma \nu_0 b \sqrt{2\pi \ln 2}}$$

The expression (15) shows that only part of the molecules of the beam,

which leave the slot source, can be used to observe the rotational lines.

If there are K vertical slots of area a in the source, then the following number of active molecules will flow through the waveguide:

$$(16) \quad N_{\text{act}} = \beta K N_{Jv} \frac{h\nu}{kT}$$

where β is the use coefficient of the molecular beam determined by (15) and the geometry of the apparatus.

The amount of energy absorbed by these molecules equals, according to (10),

$$(17) \quad E = 0.43 \beta K N_{Jv} \frac{(h\nu)^2}{kT}$$

According to (11), for this absorption of energy to be observed, the condition

$$(18) \quad P_n < \frac{E^2}{4P_{\text{opt}}}$$

must be fulfilled. The quantity P_{opt} is determined by (13).

As an example, let us consider the possibility of observing the rotational transition $J = 1 \rightarrow J = 2$ of a molecule of CsF . Let $K = 200$; $\beta = 0.03$; $a = 0.01 \text{ cm}^2$; $b = d = 1 \text{ cm}$; $n = 10^{15}$; $|\mu_2^1| = \frac{2}{3} \mu_0^2$; $\mu_0 = 7.3 \cdot 10^{-18} \text{ CGSE}$; $\nu = 17700 \text{ mc}$; $T = 850^\circ \text{ C}$, $F = 40$, $\Delta f = 0.1 \text{ cps}$. Then $\Delta\nu = 7 \text{ kc}$; $E = 3 \cdot 10^{-12} \text{ W}$; $P = 5 \cdot 10^{-8} \text{ W}$; $P_n = 2 \cdot 10^{-22} \text{ W}$; $\Delta P_{\text{min}} = 6 \cdot 10^{-14} \text{ W}$.

Therefore, a 50 times increase of signal over noise can be expected.

The spectroscope described here used up 75 gr. of substance in one hour.

In the computations cited above, the possibility was not taken into account of sorting the molecules by rotational states. The use of molecules sorted into states is considered below when a cavity resonator is used as the absorbing cell.

4. Spectroscope with a cavity resonator

As absorbing cell, let a rectangular resonator be used, in which H_{011} oscillation is excited. If a molecular beam passes through this resonator in the ox direction, then there will not be any Doppler broadening of the spectral lines since the phase velocity of the electromagnetic wave propagation will be infinite in this direction.

If a divergent beam be used, then it is necessary that the Doppler width of the line because of the v_y and v_z velocity components should be less than the width of the line specified by the time for the molecule to pass through the resonator, i.e.,

$$(19) \quad v_r = \sqrt{v_y^2 + v_z^2} < \frac{c}{\pi r \nu_0 \sqrt{2\pi \ln 2}}$$

Therefore, the admissible beam scattering angle is determined by the condition

$$(20) \quad \tan \alpha < \frac{v_r}{v} = \frac{c}{\pi r \nu_0 \sqrt{2\pi \ln 2}}$$

In deriving (19) and (20) it was assumed that the phase velocity of the wave in the oy direction equals the phase velocity of the wave in the oz direction.

In order to sustain the optimum field density $\rho(\nu)$ within the cavity resonator, it is necessary to introduce the energy P_{opt} into the resonator:

$$(21) \quad P_{opt} = \frac{2\pi\nu\rho(\nu)bd\ell}{Q} = \frac{3h^2(\Delta\nu)^2\nu db\ell}{2Q|\mu_n^m|^2}$$

where Q is the quality of the resonator.

In the derivation of (21), the energy was considered to be distributed uniformly over the cavity resonator. As seen from (21), introducing the energy into the resonator decreases the growth of Q proportionally. Consequently, as follows from (11), in order to increase the sensitivity of the spectroscope the Q of the resonator must be increased. In order to obtain a high Q in

the resonator, it is necessary to eliminate the losses because of the openings in the resonator through which the molecule beam passes. This can be attained by using as a blocking filter a section of a cylindrical waveguide which has a critical wave^{length} less than the wave-length of the molecule radiation.

The Q of the resonator can be increased considerably by means of regeneration with the aid of a traveling wave tube. The Q of the resonator can also be made sufficiently high if the resonator be cooled to the superconducting state.

The number of active molecules obtained from a slot using sorting, equals

$$(22) \quad N_{\text{act}} = \beta N_{Jv}$$

where β is the use coefficient of the beam molecules determined by (20) and the geometry of the apparatus.

The amount of the energy absorbed by these molecules equals, according to (10),

$$(23) \quad E_{\text{abs}} = 0.43 \beta N_{Jv} h\nu$$

According to (11), for this absorption to be observed, it is necessary that

$$(24) \quad P_n < \frac{E_{\text{abs}}^2}{4P_{\text{opt}}}$$

The quantity P_{opt} is determined from (21). The magnitude of the noise is determined from (12).

The use of molecules sorted according to rotational states makes possible the study not only of the absorption spectrum of molecules, but the radiation spectra of molecules since it is possible to sort molecules as desired from the beam, which are either in the lower or upper state of the considered transition.

By using molecular beams in which there are no molecules in the lower state of the considered transition, a molecular generator can be made. The operating principle of a molecular generator is the following.

A sorted molecular beam, with no molecules in the lower state of the considered transition, is passed through the cavity resonator. During the time the molecules are in the cavity resonator, part of the molecules make a transition from the upper state to the lower losing energy to the cavity resonator. If the power loss within the resonator is less than the radiation power of the molecule then self-excitation approaches, wherein the power in the resonator increases to a quantity determined by the saturation effect. Therefore, self-excitation approaches, if

$$(25) \quad N_{\text{act}} h\nu < E_{\text{loss}}$$

where E_{loss} is the power loss in the cavity resonator; namely,

$$(26) \quad E_{\text{loss}} = \frac{2\pi\nu E_{\text{pop}}}{Q}$$

Assuming that the energy in the cavity resonator is distributed uniformly over the resonator, let us write E_{pop} as

$$(27) \quad E_{\text{pop}} = \rho(\nu) V$$

where V is the resonator volume.

On the basis of (25)-(27) we obtain the self-excitation condition as

$$(28) \quad N_{\text{act}} > \frac{3Vh(\Delta\nu)^2}{2Q|\mu_n^m|^2}$$

The steady state of the generator is determined by the saturation effect. The limiting amount of the power which can be obtained from such a generator is

$$(29) \quad E_{\text{max}} = \frac{1}{2} N_{\text{act}} h\nu$$

As an example let us consider the possibility of observing the rotational transition $J = 0 \rightarrow J = 1$ of a CsF molecule. A temperature of 575°K is necessary to obtain a molecular beam, wherein 0.00025 part of the total number of molecules is in the zero rotational state ($J = 0$).

A flow of 10^{14} molecules per second can be obtained for a 1° beam width. There are $6 \cdot 10^9$ of these molecules in the $J = 0, v = 0$ state. Approximately the same number of molecules are in the $J = 1, M_J = 0, v = 0$ state. Since no molecules in the $J = 0, v = 0$ state are in the beam, then the number of molecules which is found is the number of active molecules.

The maximum energy which can be radiated in the resonator equals

$$(30) \quad E_{\max} = 1.6 \cdot 10^{-14} \text{ W}$$

We find the Q of the resonator from (28), for which self-excitation is obtained:

$$(31) \quad Q > \frac{3Vh(\Delta\nu)^2}{2N_{\text{act}}|\mu_n^m|^2}$$

Let $V = 5 \text{ cm}^3$, $(\Delta\nu)^2 = 5 \cdot 10^7 \text{ sec.}^{-2}$, then in the given case

$$(32) \quad Q > 7 \cdot 10^6$$

Since it is practically impossible to make such a resonator, then self-excitation is also impossible in our case. However, in view of the beam density not being the limit by far in our case for a mean free path of 1 cm, the self-excitation region can be realized for practically-attainable Q 's which exceed the molecular beam density considerably.

For the easily-attainable $Q \sim 5 \cdot 10^3$ and for the number of active molecules $\sim 3 \cdot 10^9$, rotational transition can be studied with the help of induced radiation. Let us find the magnitude of the power which it would be necessary to have in order to create the optimum energy density for induced molecule radiation in the resonator. As a consequence of $|\mu_n^m| = |\mu_m^n|$ the magnitude of P_{opt} can be obtained from (21):

$$(33) \quad P_{\text{opt}} = 4.9 \cdot 10^{-11} \text{ W}$$

According to (24), the observed variation of the power for $F = 40$, $\Delta f = 0.1 \text{ cps}$ equals the minimum

(34)

$$\Delta P_{\min} = 2 \cdot 10^{-15} \text{ W}$$

i.e., an increase of signal over noise of 7 times is obtained for the specified beam density.

Physics Inst. P. N. LEBEDEV

January, 1954

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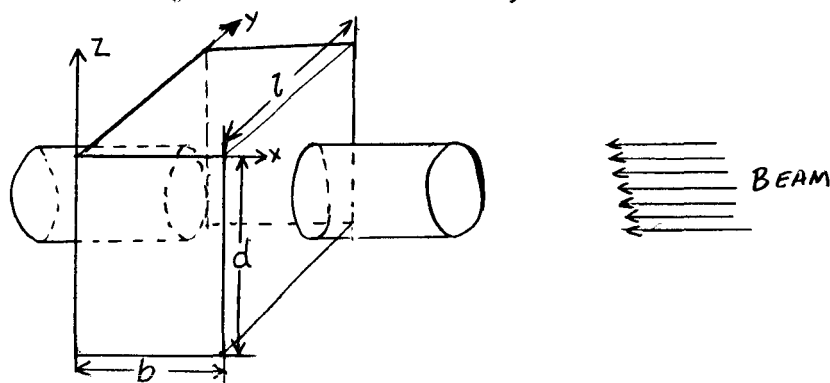


Figure 2

On Possible Methods of Obtaining Active Molecules for a Molecular Generator

N. G. BASOV & A. M. PROKHOROV

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As was shown in [1], molecular beams must be used to create high resolving power spectrometers. In the same paper, the possibility was indicated of creating a molecular generator. It was proposed to obtain the active molecules to produce the self-excitation region in the molecular generator by deflecting molecules of a beam in inhomogeneous electric or magnetic fields. Such a method of obtaining active molecules was applied in constructing a molecular generator [2].

There is still another method of obtaining active molecules: namely, the preliminary exposure of the molecular beam to an auxiliary high-frequency field causing resonance transitions between the different molecule levels. Indicated on figures 1 and 2 are possible variations of using the auxiliary radiation frequency ν_{aux} to enrich the upper level in order to obtain a self-excitation region at the frequency ν_r .

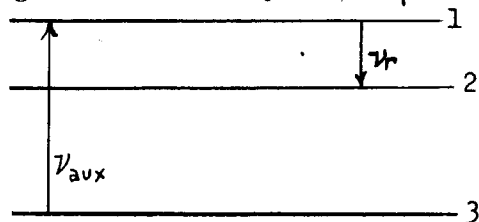


Figure 1

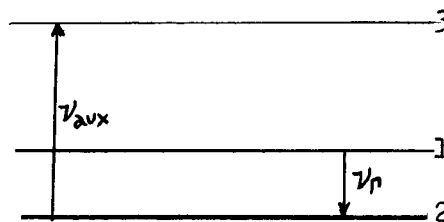


Figure 2

In the case shown in figure 1, the active molecules at the first level are obtained at the expense of the transfer of the molecules by the high-frequency field to the third level. If the high-frequency field possesses sufficient power so that a saturation effect is attained, then the number of active molecules

equals

$$(1) \quad \frac{1}{2}(N_3 - N_1) + N_1 - N_2$$

where N_i is the number of molecules at the i -th level.

The number of active molecules at the first level increases as the increase in the difference in the energy between the first and third levels relative to the difference in energy between the first and second levels. Here it should be taken into account that the number of molecules at the levels in thermal equilibrium is determined by the Boltzmann factor

$$(2) \quad N_i \sim \exp\left(-\frac{E_i}{kT}\right)$$

where E_i is the energy of the i -th level; T is the absolute temperature of the beam molecules.

The same considerations are correct in the case pictured in figure 2, only instead of an increase in the number of molecules at the first level, here there occurs a decrease in the number of molecules at the second level. In this case, the number of active molecules equals

$$(3) \quad \frac{1}{2}(N_2 - N_3) + N_1 - N_2$$

The methods we proposed can be used, for example, in the following cases.

1) Levels 1 and 2 are neighboring rotational levels belonging to the same oscillatory state of the molecule but level 3 belongs to an adjacent oscillatory state of the molecules in which the rotational quantum number of this level differs from the rotational quantum number of levels 1 and 2 by $\Delta J = 0, \pm 1$.

It is suitable to use the transitions between the oscillatory levels with the $\Delta J = \pm 1$ variation since, in this case, no very high requirements are produced on the monochromaticity of the auxiliary radiation. Because of

transitions between oscillatory levels, the majority of molecules drop into the infra-red region of the spectrum, then the auxiliary radiation must belong to this frequency range. It should be noted that the power of thermal sources of infra-red radiation in existence at present is inadequate to obtain the saturation effect.

2) Levels 1, 2 and 3 are rotational levels of the molecule of the asymmetrical gyroscope type.

3) Levels 1 and 2 are levels of superfine structure belonging to identical rotational states and level 3 is a level of superfine structure of a neighboring rotational level with respect to 1 and 2.*

4) Levels 1 and 2 are levels specified by an inversion twin belonging to identical rotational states and level 3 is one of the inversion levels of the neighboring rotational state.

The proposed methods can permit obtaining a sufficient number of active molecules to create low-frequency molecular generators.

Physics Inst., P. N. Lebedev

January. 1954

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* This method is unsuitable for linear molecules for which the transition between levels of superfine structure for $\Delta J = 0$ is forbidden.